

Self-assembly of colloids driven by disclinations in a nematic host fluid

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Abstract

We present extensive Monte Carlo simulations of a pair of colloidal particles immersed in a nematic host fluid. Through a calculation of the local director field $\hat{\mathbf{n}}(\mathbf{r})$ we show that a pair of homogeneous colloids with locally planar anchoring surfaces attract each other if their center-of-mass distance vector forms an angle of about $\theta \simeq 30^\circ$ with the far-field director $\hat{\mathbf{n}}_0$. We ascribe this attraction to a change in the complex three-dimensional defect structure building around the colloids and changing as θ varies. This result settles a long-standing discrepancy between theory and experiment. We then extend our study to investigate Janus colloids where the attraction mediated by the host phase turns out to be stronger on account of the reduced stability of the disclination topology forming near these colloids.

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If a liquid crystal is in the nematic phase the overall orientation of its molecules (i.e., mesogens) can be described quantitatively by the non-local unit vector (i.e., the director) $\hat{\mathbf{n}}_0$ [1]. Immersing a colloidal particle in this nematic host gives rise to a director field $\hat{\mathbf{n}}(\mathbf{r})$ such that sufficiently close to the colloid's surface $\hat{\mathbf{n}}(\mathbf{r})$ and $\hat{\mathbf{n}}_0$ may differ. The deviation between $\hat{\mathbf{n}}(\mathbf{r})$ and $\hat{\mathbf{n}}_0$ is caused by the specific anchoring of mesogens at the surface of the colloid. Depending on details of the host phase $\hat{\mathbf{n}}(\mathbf{r})$ can be of such dazzling complexity that experts are just beginning to unravel its structural details [2].

The mismatch between $\hat{\mathbf{n}}(\mathbf{r})$ and the far-field director $\hat{\mathbf{n}}_0$ also gives rise to effective interactions between several colloids that are mediated by the nematic host [3]. These interactions may therefore be used to self-assemble the colloids into supramolecular entities in a controlled (i.e., directed) manner. This way ordered assemblies of colloids of an enormously complex structure with rich symmetries may be built that would not exist without the liquid-crystalline nature of the host [4, 5].

The complex self-assembled structures formed by the colloids are also of practical importance. For instance, taking as a specific example dielectric colloids it could be demonstrated that the propagation of light through a self-assembled ordered colloidal arrangement is affected in a way similar to the propagation of electrons in a semiconductor crystal [6]. Hence, ordered periodic assemblies of colloids are already discussed within the framework of novel photonic devices with fascinating properties [7].

Clearly, in order to use the effective interaction potential to self-assemble colloids in a nematic host phase the molecular origin of the potential must be understood. Our motivation to contribute to such an improved understanding goes back to an observation made some time ago by Poulin and Weitz [8] who found experimentally that if a pair of colloids is suspended in a nematic host fluid they arrange themselves such that their center-to-center distance vector \mathbf{r}_{12} forms an angle of $\theta \approx 30^\circ$ with $\hat{\mathbf{n}}_0$ if the mesogens at the surfaces of the colloidal pair are anchored in a locally planar fashion.

This experimental observation resisted a quantitative theoretical explanation to date. In previous theoretical attempts a much larger angle of about 50° is usually found [8, 9]. This number is based upon calculations where one employs the electrostatic analog of the Boojum [10] defect topology that evolves if one suspends a pair of colloids with locally planar surface anchoring in a nematic host phase [8]. In fact, as stated explicitly by Poulin and Weitz “This theoretical value is different from the experimentally observed value for θ ... since

the theory is a long-range description that does not account for short-range effects” [8]. Another motivation for our work is the more recent experimental observation that between a pair of colloids in a nematic host repulsive and attractive forces act depending on θ [9]. For example, at $\theta \approx 30^\circ$ the colloids attract each other whereas at $\theta = 0^\circ$ and 90° repulsion between the colloids is observed.

To unravel the persisting discrepancy between theory and experiment we employ Monte Carlo (MC) simulations to investigate the effective interaction between a pair of spherical, homogeneous colloids mediated by a nematic host phase. We take the radius of a colloid to be $r_0 = 3$ (given in units of the “diameter” σ of a mesogen). The colloids are fixed in space such that no *direct* interaction between them needs to be considered. At the surface of each colloid mesogens are anchored in a locally planar fashion such that at a *single, isolated* colloid the well-known Boojum defect topology evolves (see, for instance, Fig. 6 of Ref. 11), that is regions of low nematic order exist at the North and South Pole of a colloid where the planar orientation of the mesogens is orthogonal to $\hat{\mathbf{n}}_0 = (1, 0, 0)$. Throughout this work we fix this $\hat{\mathbf{n}}_0$ by placing the nematic host plus colloidal pair between planar, structureless solid surfaces at which mesogens are always anchored along the x -axis. The solid surfaces are separated sufficiently so that they do not directly interfere with mesogens near the colloids. Colloids are placed equidistantly from both substrates and such that $\mathbf{r}_{12} = (x_{12}, y_{12}, 0)$. Conditions of the simulations, the form of our model potentials, specific values of their parameters, and thermodynamic conditions for the Boojum defect topology are chosen as in our previous work [11].

We compute $\hat{\mathbf{n}}(\mathbf{r})$ as the eigenvector associated with the largest eigenvalue $\lambda(\mathbf{r})$ of the local alignment tensor

$$\mathbf{Q}(\mathbf{r}) \equiv \frac{1}{2\rho(\mathbf{r})} \left\langle \sum_{i=1}^N [3\hat{\mathbf{u}}(\mathbf{r}_i) \otimes \hat{\mathbf{u}}(\mathbf{r}_i) - \mathbf{1}] \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle \quad (1)$$

where ρ is the local density, $\hat{\mathbf{u}}$ is a unit vector specifying the orientation of mesogen i located at \mathbf{r}_i , δ is the Dirac δ -function, \otimes represents the tensor product, $\mathbf{1}$ is the unit tensor, and $\langle \dots \rangle$ indicates an ensemble average. Similarly, we obtain $\hat{\mathbf{n}}_0$ from the nonlocal analog of \mathbf{Q} using Jacobi’s method [12] in both cases.

Regions of the host fluid in which $|\hat{\mathbf{n}}(\mathbf{r}) \cdot \hat{\mathbf{n}}_0| < 1$ give rise to attractive or repulsive *effective* interactions between the colloidal pair and transmitted by the nematic host. We

analyze these interactions by considering the local Frank free-energy density

$$\frac{2f(\mathbf{r}; \mathbf{r}_{12})}{K} = [\nabla \cdot \hat{\mathbf{n}}(\mathbf{r}; \mathbf{r}_{12})]^2 + [\nabla \times \hat{\mathbf{n}}(\mathbf{r}; \mathbf{r}_{12})]^2 \quad (2)$$

in one-constant approximation where K is a material constant [1]. Without this approximation one would have three such constants K_1 , K_2 , and K_3 associated with splay, twist, and bend deformations of $\hat{\mathbf{n}}(\mathbf{r}; \mathbf{r}_{12})$, respectively. However, using the method of Allen and Frenkel [13, 14] we verified that all three constants are about the same and that they are in the right ballpark with respect to a large number of liquid crystals (see Table 3.2 of Ref. 1). The notation used in Eq. (2) emphasizes that f at point \mathbf{r} also depends on the (fixed) separation \mathbf{r}_{12} of the colloidal pair. Hence, integrating f over $d\mathbf{r}$ gives the *total* Frank free-energy $\mathcal{F}(\mathbf{r}_{12}) > 0$ depending on the configuration of the colloidal pair. In practice, we compute $\mathcal{F}(\mathbf{r}_{12})$ by first evaluating Eq. (2) numerically using $\hat{\mathbf{n}}(\mathbf{r}; \mathbf{r}_{12})$ from MC and subsequent integration of the resulting $f(\mathbf{r}; \mathbf{r}_{12})$ by a standard trapezoidal rule.

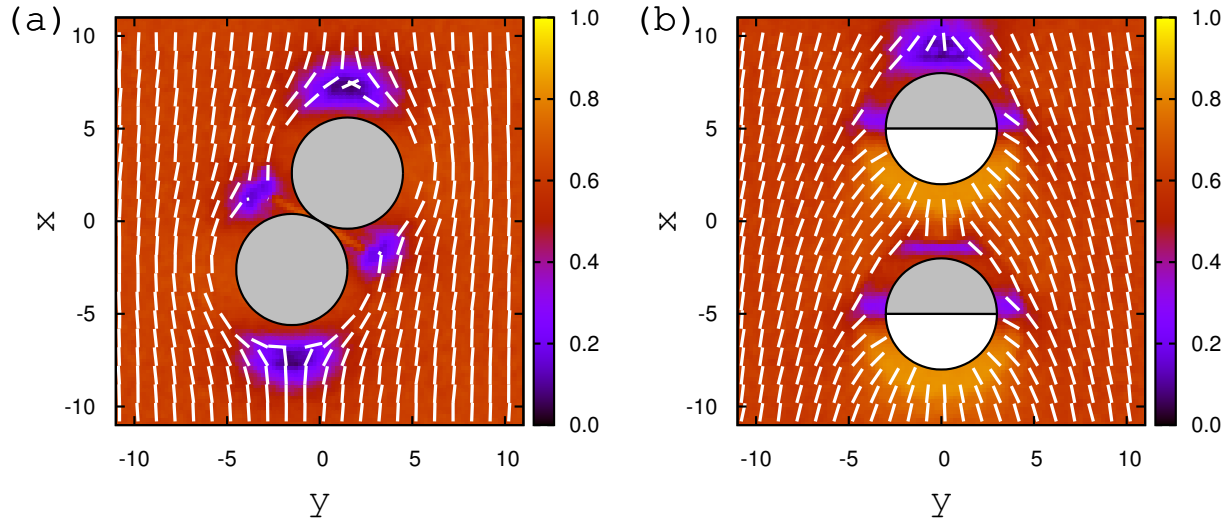


FIG. 1. (Color online) Plots of $\lambda(\mathbf{r})$ (see color bar) and $\hat{\mathbf{n}}(\mathbf{r})$ (dashes) in the x - y plane for a colloidal pair (circles). (a) Homogeneous colloids with locally planar anchoring of mesogens ($\theta = 30^\circ$); (b) Janus colloids with locally planar (gray) and homeotropic (white) anchoring hemispheres ($\theta = 0^\circ$).

Fig. 1(a) shows a plot of $\lambda(\mathbf{r})$ and $\hat{\mathbf{n}}(\mathbf{r})$ for a colloidal pair where \mathbf{r}_{12} forms an angle of $\theta = 30^\circ$ with $\hat{\mathbf{n}}_0$. Sufficiently far away from the colloids the liquid-crystal host phase is nematic under the thermodynamic conditions chosen as one infers from the attached color

bar [11]. At the surfaces of both colloids mesogens are anchored in a locally planar fashion. The plot indicates that at the North Pole of the upper ($x_{12} > 0$) and at the South Pole of the lower colloid ($x_{12} < 0$) regions exist where $\lambda(\mathbf{r})$ is much smaller than sufficiently far away from the colloidal pair. These regions of low nematic order, which arise because of the mismatch between the local planar anchoring and $\hat{\mathbf{n}}_0$, are remnants of the Boojum defect topology. Therefore, at sufficiently large distances $r_{12} = |\mathbf{r}_{12}|$ one anticipates a regular Boojum defect topology. However, because $r_{12} = 2r_0$ in Fig. 1(a) part of the Boojum defect topology has shifted towards the equators of the colloids and decreased in size.

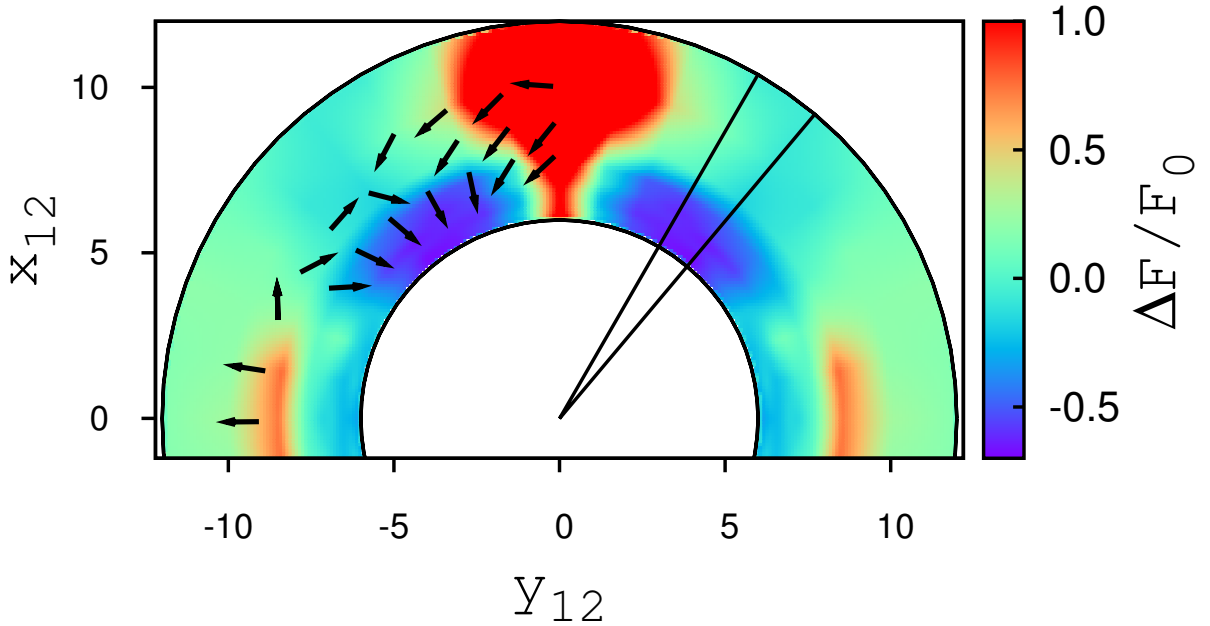


FIG. 2. (Color online) Plots of the ratio $\Delta\mathcal{F}/\mathcal{F}_0$ (see color bar) and associated force (arrows) for different configurations \mathcal{C} of a colloidal pair. The sector demarcates the range of angles $30^\circ \lesssim \theta \lesssim 40^\circ$ between \mathbf{r}_{12} and $\hat{\mathbf{n}}_0$ where $\Delta\mathcal{F}$ is smallest. The white area at the center is the volume excluded to the colloids.

From plots similar to the one in Fig. 1(a) but for different configurations of a colloidal pair in the x - y plane we extract \mathcal{F} according to the procedure outlined above. However, instead of analyzing \mathcal{F} directly (which is positive definite by definition) we consider $\Delta\mathcal{F} \equiv \mathcal{F} - 2\mathcal{F}_0$ where \mathcal{F}_0 is the Frank free energy for a *single, isolated* colloid. The plot of $\Delta\mathcal{F}$ in Fig. 2 reveals attractive and repulsive regions where, in particular, the maximum attraction arises for $30^\circ \lesssim \theta \lesssim 40^\circ$ in nearly quantitative agreement with *experimental* findings [8, 9]. Moreover, for $\theta = 0^\circ$, Fig. 2 reveals strong repulsion between the colloids. This is in

disagreement with the Landau-de Gennes theory of Tasinkevych *et al.* who predict an attraction if r_{12} is small enough [15].

Suppose now we do the following *Gedankenexperiment*. Place two colloids in a fixed configuration $\mathcal{C} = (r_{12}, \theta)$ such that $r_{12} \geq 2r_0$ which could be done in a real experiment by using, for instance, optical tweezers [9]. If one of the colloids is released at fixed initial r_{12} the second colloid would move in the direction of the effective local force as indicated by the arrows in Fig. 2. Hence, if released at about $\theta \simeq 90^\circ$ and $|r_{12}| \gtrsim 9\sigma$ the colloid would move away from the fixed one at the center in a radial direction; if, on the contrary, the initial separation is chosen such that $|r_{12}| \lesssim 8\sigma$ the released colloid would start its motion in a region where $\Delta\mathcal{F}$ is attractive and surrounded by regions of higher $\Delta\mathcal{F}$. Under these conditions the released colloid would simply stay put. However, if released at $\theta \simeq 0^\circ$ the trajectory of the colloid is more complex. It first moves out of the repulsive region in a more or less lateral direction. Moving in the direction indicated in Fig. 2 the colloid eventually reaches a region where $\Delta\mathcal{F}$ becomes attractive. Its motion then changes direction and the colloid is pulled towards the minimum of $\Delta\mathcal{F}$ in an increasingly radial direction as r_{12} becomes smaller. Finally, the colloid at rest is approached at $30^\circ \lesssim \theta \lesssim 40^\circ$ until r_{12} corresponds to the minimum of $\Delta\mathcal{F}$. These hypothetical trajectories for the two values of θ are in agreement with experimental results depicted in Fig. 2(b) of Ref. 9. Thus, we conclude that also the topography of $\Delta\mathcal{F}$ shown in Fig. 2 is correct.

To rationalize the variation of $\Delta\mathcal{F}$ we consider in Fig. 3 the development of regions of low nematic order as θ varies. To visualize these regions we divide the simulation cell into cubic boxes of side length $\delta s = 0.20\sigma$ and color the entire box red if $\lambda(\mathbf{r}) \leq 0.25$. This admittedly somewhat arbitrary value has been chosen because in practice it turned out to optimize the visibility of the rather complex three-dimensional structural changes. Because the colloids touch each other the regions of low $\lambda(\mathbf{r})$ characteristic of a Boojum defect and located at the South and North Poles of the respective upper and lower colloid have merged in Fig. 3(a) and form a torus. As θ increases the toroidal structure is gradually deformed [see Figs. 3(b) and 3(c)]. Eventually, at $\theta = 30^\circ$ [see Fig. 3(d)] and $\theta = 40^\circ$ [see Fig. 3(e)] the torus disappeared and four fairly small, disconnected, and localized regions remain in which $\lambda(\mathbf{r}) \leq 0.25$. For $\theta > 40^\circ$ these regions start to grow in size and eventually merge to form a “handle” on top and bottom of the colloidal pair for $\theta > 60^\circ$.

In general, low values of $\lambda(\mathbf{r})$ imply a stronger spatial variation of $\hat{\mathbf{n}}(\mathbf{r})$ which causes

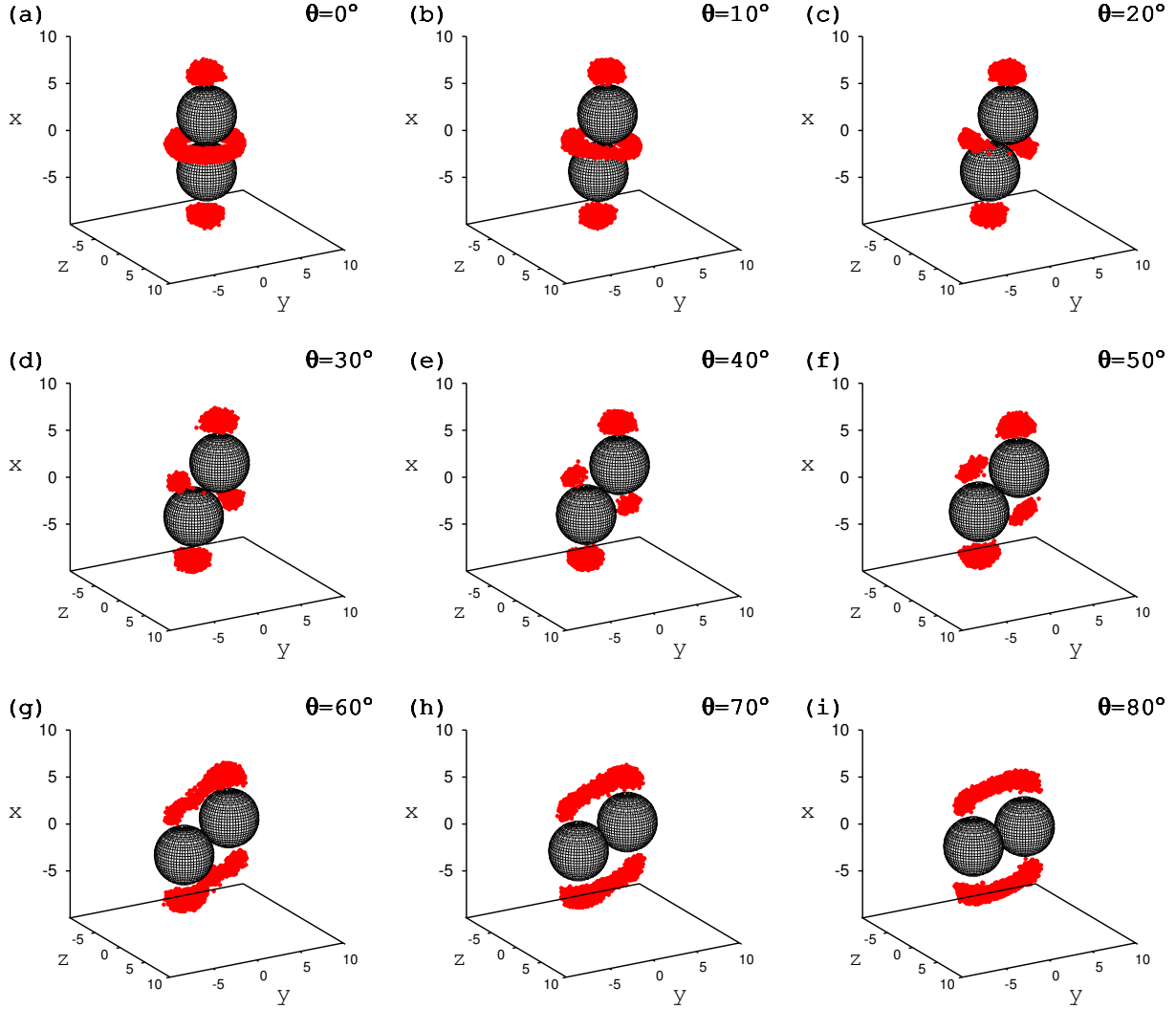


FIG. 3. Configurations $\mathcal{C}(2r_0, \theta)$ of a colloidal pair as a function of angle θ between distance vector and x -axis. Areas shaded in red correspond to regions where $\lambda(\mathbf{r}) \leq 0.25$.

the Frank free energy to increase. Therefore, the bigger these regions of low $\lambda(\mathbf{r})$ the larger is $\Delta\mathcal{F}$. Let N be the number of boxes colored in red which is proportional to the volume of the defect region in the plots in Fig. 3 and let M have a similar meaning for a single, isolated Boojum defect topology. Then $\Delta\mathcal{V} = N/M - 2$ is a measure of the volume of defect regions plotted in Fig. 3 *relative* to the equivalent volume of the Boojum defect regions near two single colloids. Moreover, according to the above line of arguments, $\Delta\mathcal{V}$ is proportional to $\Delta\mathcal{F}$. The plot in Fig. 4 shows that $\Delta\mathcal{V} < 0$ except for $\theta \simeq 0^\circ$. This indicates that the size of the defect region near a single colloid almost always exceeds that near a colloidal pair

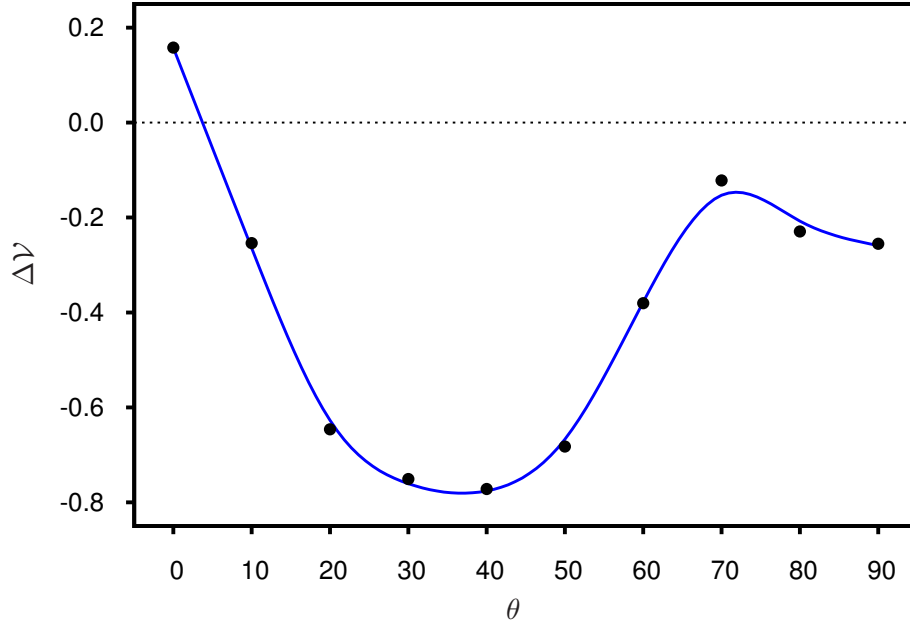


FIG. 4. (Color online). Plot of the relative volume of the defect region $\Delta\mathcal{V}$ (see text) as a function of the angle θ . The blue line is a fit intended to guide the eye.

(note that $\Delta\mathcal{V} < 0$ does *not* imply $\Delta\mathcal{F} < 0$). Moreover the curve plotted in Fig. 4 passes through a minimum for $30^\circ \lesssim \theta \lesssim 40^\circ$ which correlates nicely with the plot of $\Delta\mathcal{F}$ in Fig. 2.

In addition to the homogeneous colloidal pair we also consider Janus colloids in this letter. Janus colloids are nm- to μm -size particles consisting of moieties with antithetic properties. Due to advances in chemical synthesis they can nowadays be fabricated with well defined boundaries separating these moieties. Here we consider spherical Janus colloids where one hemisphere aligns mesogens in a locally homeotropic fashion whereas the local alignment at the other hemisphere is planar. Were the Janus colloids sufficiently far apart a Boojum ring defect topology would evolve [16]. Again, conditions of the MC simulations are identical to those chosen in Ref. 11.

To make contact with experimental data [see Fig. 7(a) of Ref. 16] we consider a pair of Janus colloids in a configuration in which the vectors pointing from the homeotropically aligning hemisphere to the planar aligning one are always parallel to each other and parallel with $\hat{\mathbf{n}}_0$. This configuration is particularly interesting because the plot in Fig. 1(b) shows that the homeotropically aligning lower hemisphere of the upper colloid is capable of inducing enhanced nematic order at the North Pole of the lower Janus colloid and hence destroys the

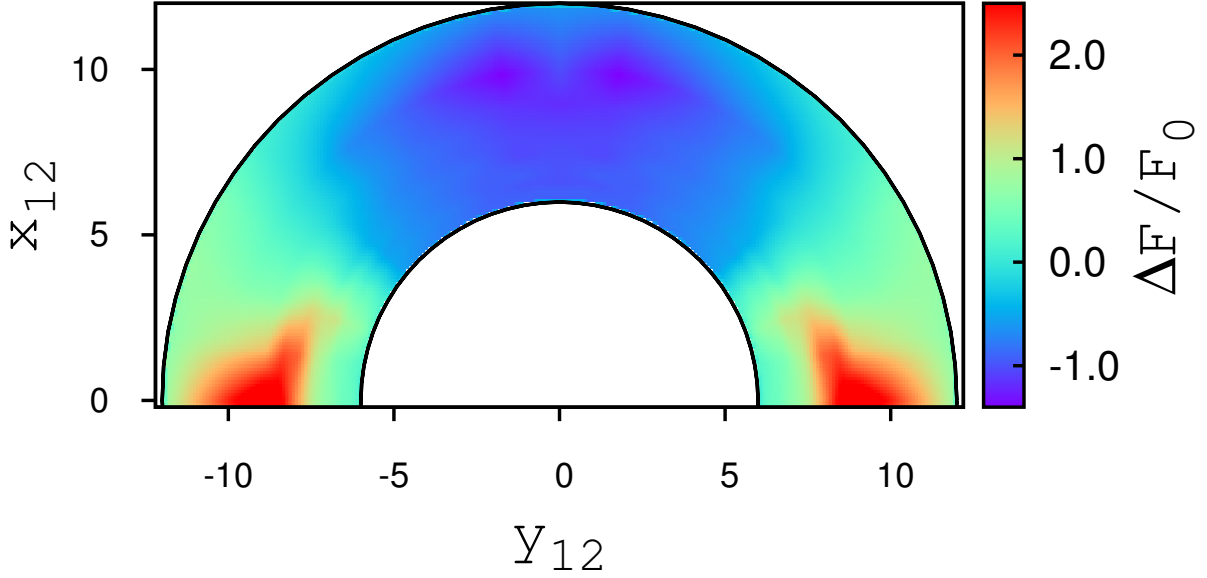


FIG. 5. As Fig. 2, but for a pair of Janus colloids in the configuration shown in Fig. 1(b).

Boojum ring topology at this latter colloid. At the upper colloid the Boojum ring topology remains undisturbed.

The corresponding plot in Fig. 5 reveals that broad regions exist in which the Janus colloids attract each other. These regions are a result of the partial destruction of one of the two Boojum ring defect topologies and the simultaneous enhancement of local nematic order which arises if the Janus colloids are in a collinear configuration. If, on the other hand, the Janus colloids are arranged in a side-side configuration regions of low nematic order on top of both colloids and around them merge similar to what we saw before in Figs. 3(g)–3(i). As a result repulsive barriers are observed in the plot of $\Delta\mathcal{F}$ in Fig. 5. Another interesting feature visible in Fig. 5 is that the minimum of $\Delta\mathcal{F}$ is shifted to distances $r_{12} > 2r_0$ at which the colloids do not touch. On the contrary, for the homogeneous colloid the minimum occurred for $r_{12} \approx 2r_0$.

Hence, by tuning the strength of the homeotropic anchoring of mesogens at the colloids' lower hemispheres one would move the attractive well of $\Delta\mathcal{F}$ to different r_{12} 's. One could therefore envision stable configurations of Janus colloids at variable r_{12} by “simply” tuning their surface chemistry.

To summarize, we compute the effective interaction between two homogeneous, spherical colloidal particles immersed in a nematic host phase. The effective interactions are mediated

by the host through a deviation of the local director field $\hat{\mathbf{n}}(\mathbf{r})$ from its nonlocal far-field counterpart $\hat{\mathbf{n}}_0$. Our simulations are the first theoretical work in which the experimentally well-known [8, 9] formation of an angle $\theta \approx 30^\circ$ between \mathbf{r}_{12} and $\hat{\mathbf{n}}_0$ is confirmed quantitatively. Our results confirm the conjecture of Poulin and Weitz who suspected that the observation of this particular range of angles must be a short-range effect [8].

This “magic” angle arises as a result of a complex three-dimensional change in defect topology. At small θ defect regions first dissolve, assume a minimum size over a range $30^\circ \lesssim \theta \lesssim 40^\circ$, and then start to grow again for $\theta > 40^\circ$. The stability of defect topologies determines the magnitude of the effective attraction mediated: if a particular topology forming near a single, isolated colloid is relatively easy to destroy or can be weakened by the presence of a neighboring colloid then the minimum in the effective potential is deeper. This turns out to be the case for Janus colloids where the Boojum ring topology is less stable than the Boojum topology forming near a homogeneous colloid [11].

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